EFFECTIVE CORE POTENTIAL STUDY OF SOME HEAVY METAL COMPOUNDS

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ABSTRACT

Computational chemistry gives insight into many chemistry problems. Chemistry of heavy metals is a fascinating one in the field of chemistry. Effective core potential methods are available to model heavy metals. Due to time and space small molecules are modelled to imitate bigger molecules. In this work heavy metal salts like mercury iodide, mercury oxide, cadmium chloride silver nitrate, copper nitrate and titanium dioxide were modelled by DFT/B3LYP/SBKJC in gas phase at 25°C. The resulting electronic and structural parameters are compared with macroscopic properties. It was found that TiO_2 is non-linear and atomic size influences the charge density and structural parameters. Dipole moment gave information about the orientation of atoms in the molecule. FMO studies reveal that the ionisation of electron takes place from the non-metals and election affinity depends on the metals. Melting point depends on charge density.

KEYWORDS: DFT, SBKJC, ECP, d-block, metal compounds, computation.

1. INTRODUCTION

Behaviour of a compound can be determined by the chemistry of its microscopic domain. The microscopic domain can be understood through mathematics as theoretical study by utilising computers. In the midst of many methods, DFT gives good results. Bigger atoms can be modelled using effective core potential method (Xu and Truhlar, 2012). Due to higher computational cost, small compounds are modelled in the place of bigger atoms, to study their chemistry as well to correlate with their macroscopic properties (Young, 2004). Heavy metals play a crucial role in the chemistry, biology and environment (Sarkar, 2005). Some of the important heavy metals are mercury, cadmium, copper, silver and titanium (Bradl, 2005).

Mercury oxide has orthorhombic and hexagonal structures through Hg-O chain (Aurivillius *et. al.*, 2010). DFT calculations of energetics, oligomerization and solvation of HgO in gas phase reveals that oligomers with ring structure of n=4-6 are stable and 6 member are more stable (Tossell, 2006). Quantum mechanical studies of large metal, metal oxide, and metal chalcogenide nanoparticles and clusters were reviewed (Fernando et. al., 2015). Atmospheric mercury depletion events are higher at the dead sea due to the presence of BrO (Moore et. al., 2013). Bonding in mercury for HgX and cationic HgX^+ type small components using couple cluster method showed that mercury undergoes weak covalent bonding with its partner X in most cases, which lead to van der Waals bonding (Cremer *et. al.*, 2008).

Electronic structure through DFT, HF and Compton profiles of CdO and HgO infer that HF predicted higher value, while DFT gives comparable values with experiment (Choudhary *et. al.*, 2011). Review of computational methods concluded that heterogeneous and adsorption methods have efficient removal of HgO (Ling *et.al.*, 2015). The pros and corns of silver, cadmium and titanium were well documented (Alloway, 2005). Review on use of cadmium chloride in solar cell gave understand about its function (Dharmadasa, 2014). Electric field gradient study in cadmium complex using DFT/B3LYP, HF and MP2 methods gave variable results with experiment (Antony *et. al.*, 2000). Aqueous microsolvation of $CdCl_2$ and $HgCl_2$ by B3PW91/6-31G** and Born-Oppenheimer molecular dynamics studies reveal that unlike $HgCl_2-(H_2O)_n$ has three water molecules while, Cd establishes four equatorial orbital interactions with water for $n > 6$ leading to a planar square bipyramid hexacoordination around Cd (Solís and Marol, 2014).

Mercuric iodide can be used as a semiconductor X-ray detector for computed tomography (Beinglass *et. al.*, 1980). *Ab initio* effective core potential calculations were done for HgI_2, PtI_2, and PbI_2(Howard, 1994). Titanium dioxide and silver nitrates have photo sensing behaviour. Understanding about the photocatalytic activities of TiO_2 were reviewed (Schneider *et. al.*, 2014). Numerous computational studies are available for silver salts (Soriano and Contelles 2006). DFT, TDDFT and crystallographic study of copper complex with polypyridile expose that around copper the geometry was distorted trigonal bipyramidal (Patel *et al.*, 2016).

The present study aims to report the effective core potential study of some heavy metal salts viz. mercury iodide, mercury oxide, cadmium chloride silver nitrate, copper nitrate and titanium dioxide by DFT/B3LYP/SBKJC. The computed parameters were compared with their experimental physical properties obtained from the literature.

2. COMPUTATION

The computations were performed by density function theory using B3LYP method and SBKJC basis set at 25°C in gas phase.

3. RESULTS AND DISCUSSION

Chemistry of materials can be explained with two major theories and hybrid of these two theories. The first one is centred around the mass and second is of electronic in nature. Concentrations are based on mass and hydride theories are valence and steric effects. Electronic effects can be explained through hybridisation, molecular orbital, FMO and quantum theories. Though theories be able to explain the chemistry, the parameters are the measurable forms. In this work an attempt has been made to explain the bulk properties through electronic and steric effects .

3.1 Structure

Structure confines the electrons on the bond based on hybridisation theory. The 2-D, 3-D structures and numbering pattern of the heavy metal compounds are given in Fig.1 and their geometrical parameters are given in Table 1. Except TiO_2 other mono and diatomic compound are nearly planar. The metal to nitrates bond angle in nitrates are 90°. Bond lengths are mainly governed by the size and nature of hybridisation. Dihedral angles give the special arrangement. The two nitro groups in copper nitrate are perpendicular to each other to avoid steric effect.

3.2 Charge Density

Charge density measures the localisation of electron in an atom. All the metals and non-metals have positive and negative charges respectively. The charges are governed by size and polarizability of the counter atom. The charges are presented in Table 2.

3.3 Dipole moment

The dipole moment is given in Table 3. It gives the information about the charge localisation in a molecule. The diatomic and balanced molecules has nearly zero dipole moment, while others are having very high dipole moment. Due to the angular nature TiO_2 has non-zero and higher dipole moment. Silver nitrate has highest dipole moment and HgO has third highest dipole moment. Though they are derivatives of oxygen, the special arrangement and the presence of nitrogen is the cause of higher dipole moment in the nitrate. HgO has higher electron cloud along the π-bond direction. Silver nitrate and TiO_2 have higher value along the molecular axis. This can be attributed for the angular nature of the molecules.

3.4 Frontier Molecular Orbital

The FMO diagrams and data are given in Fig.1 and Table 4. In order to overcome the draw backs of hybridisation theory MO theory emerged. MO theory has the basis as, electrons are not confined to the bonds as in the case of hybridisation but, they are in the molecular orbitals. Over the time it was understood that most of the MOs are not significantly involve in the chemistry of molecules but only the MOs in the forefront are significant. Theory based on frontier MOs is called Frontier Molecular Orbital (FMO) Theory. The FMO gives importance to HOMO and LUMO. All the HOMO and LUMO are stable. Here the HOMO is centred near the electron rich non-metals and LUMO is at the metal. This explains that ionisation potential takes up electron from the non-metals and electron affinity is for metals.

Band gap reveals that electrical conductance of HgO is high and CdCl$_2$ is low. Oxide and copper are highly conducting than iodide and silver. All the compounds have high ionisation potential (IP) and low electron affinity (EA) and the standard deviation for IP is low when compared to EA. Nascent electron donating and electron accepting character in the molecule are higher for copper salt. The compounds are chemically less stable and soft with comparable values. Electrophilicity is higher for cadmium salt and least for HgO. Copper has very high electron donating capacity and cadmium has the least.

3.5 Pearson's Correlation Studies

Pearson's coefficients were calculated for the physical properties and the computed parameters. The values are given in Table 5. There is high positive correlation between HOMO and magnetic susceptibility. Charges on metals are directly related to charge on non-metals. Further charge on metal is positively related dipole moment. HOMO-LUMO; Density-Charge on non-metal; melting point-charge on metal have moderate positive correlation.

4. CONCLUSION

Effective core potential study of some heavy metal salts were carried out. The relationship between the computed values and some physical properties are compared. TiO$_2$ has non-linear structure. The two nitro groups in the copper are opposite to each other. Metals have positive and non-metals have negative charge. Most of the salts have low dipole moment. Their FMOs are stable. Cadmium salt has higher conductance. HOMO and charge on non-metals determine the magnetic susceptibility and charge on metals respectively.

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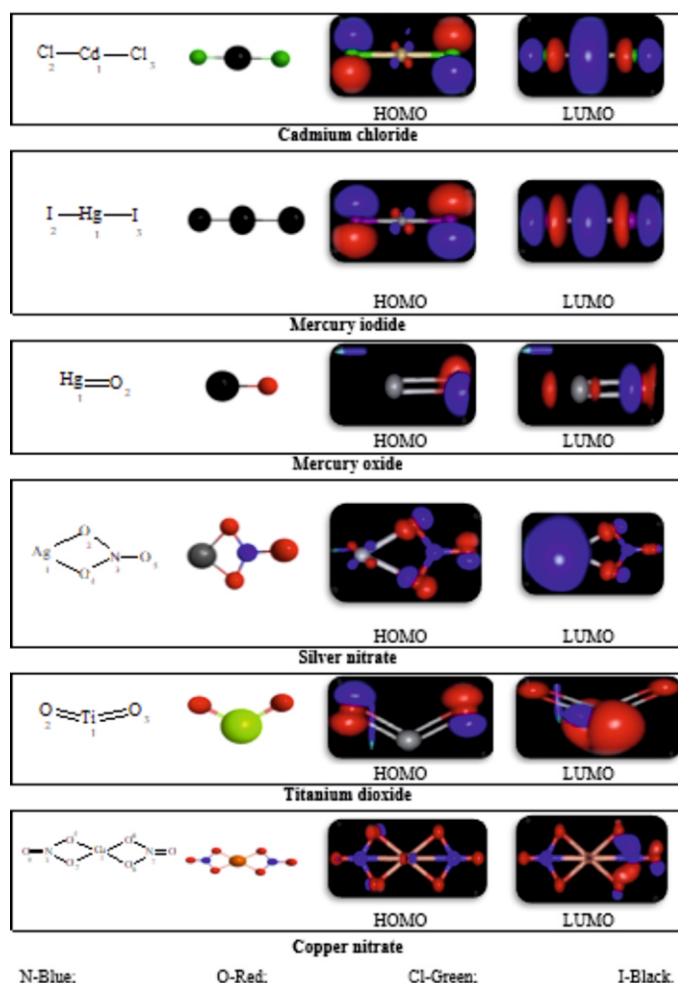4. Beinglass, I, Kaufman, L, Hoisier, K and Hoenninger, J. (1980), Medical Physics, 7, p. 370-373.
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N-Blue;   O-Red;   Cl-Green;   I-Black.

Figure 1: 2-D,3-D Structures, Numbering Pattern and FMO

Table 1: Geometrical Parameters

Cadmium chloride			
Atom Pair	**Bond Length (Å)**	**Atom Pair**	**Bond Angle (°)**
Cd$_1$-Cl$_2$	2.3425	Cl$_2$-Cd$_1$-Cl$_3$	179.948
Cd$_1$-Cl$_3$	2.3425		

Mercury iodide			
Atom Pair	**Bond Length (Å)**	**Atom Pair**	**Bond Angle (°)**
Hg$_1$-I$_2$	2.6673	I$_2$-Hg$_1$-I$_3$	179.952
Hg$_1$-I$_3$	2.6673		

Mercury oxide	
Atom Pair	**Bond Length (Å)**
Hg$_1$-O$_2$	1.9900

Silver nitrate					
Atom Pair	**Bond Length (Å)**	**Atom Pair**	**Bond Angle (°)**	**Atom Pair**	**Dihedral (°)**
Ag$_1$-O$_2$	2.3256	Ag$_1$-O$_2$-N$_3$	92.490	Ag$_1$-O$_2$-N$_3$-O$_5$	-180
O$_2$-N$_3$	1.3533	O$_2$-N$_3$-O$_4$	115.870	O$_5$-O$_2$-N$_3$-O$_4$	-180
N$_3$-O$_5$	1.2737	O$_2$-N$_3$-O$_5$	122.071		
N$_3$-O$_4$	1.3533				

Titanium dioxide			
Atom Pair	**Bond Length (Å)**	**Atom Pair**	**Bond Angle (°)**
Ti$_1$-O$_2$	1.6620	O$_2$-Ti$_1$-O$_3$	111.676
Ti$_1$-O$_3$	1.6621		

Copper nitrate					
Atom Pair	**Bond Length (Å)**	**Atom Pair**	**Bond Angle (°)**	**Atom Pair**	**Dihedral (°)**
Cu$_1$-O$_2$	2.0003	Cu$_1$-O$_2$-N$_3$	90.58	Cu$_1$- O$_2$-N$_3$-O$_4$	0.00
Cu$_1$-O$_6$	2.0005	Cu$_1$-O$_6$-N$_7$	90.58	Cu$_1$- O$_2$-N$_3$-O$_5$	-180.00
O$_2$-N$_3$	1.3673	O$_2$- Cu$_1$-O$_6$	179.96	Cu$_1$-O$_6$-N$_7$-O$_8$	0.00

Copper nitrate					
Atom Pair	**Bond Length (Å)**	**Atom Pair**	**Bond Angle (°)**	**Atom Pair**	**Dihedral (°)**
N$_3$-O$_4$	1.3673	O$_2$-N$_3$-O$_4$	110.51	Cu$_1$-O$_6$-N$_7$-O$_9$	-180.00
N$_3$-O$_5$	1.2500	O$_2$-N$_3$-O$_5$	124.75	O$_2$- Cu$_1$-O$_6$-N$_7$	83.85
O$_6$-N$_7$	1.3673	O$_4$-N$_3$-O$_5$	124.75	N$_3$-O$_2$- Cu$_1$- N$_7$	180.00
N$_7$-O$_8$	1.3673	O$_6$-N$_7$-O$_8$	110.50		
N$_7$-O$_9$	1.2500	O$_6$-N$_7$-O$_9$	124.75		

Table 2: Mullikan's Atomic Charge Density

Cadmium chloride		Mercury iodide		Mercury oxide		Silver nitrate		Titanium dioxide		Copper nitrate	
Atom	**Charge**	**Atom**	**Charge**	**Atom**	**Charge**	**Atom**	**Charge**	**Atom**	**Charge**	**Atom**	**Charge**
Cd_1	0.6190	Hg_1	0.1518	Hg_1	0.4192	Ag_1	0.5516	Ti_1	0.7450	Cu_1	0.3114
Cl_2	-0.3095	I_2	-0.0759	O_2	-0.4192	O_2	-0.1951	O_2	-0.3725	O_2	-0.0869
Cl_3	-0.3095	I_3	-0.0759			N_3	-0.1101	O_3	-0.3725	N_3	-0.0357
						O_4	-0.1952			O_4	-0.0869
						O_5	-0.0513			O_5	0.0538
										O_6	-0.0869
										N_7	-0.0357
										O_8	-0.0869
										O_9	0.0538

Table 3: Dipole moment

	Dipole moment (D)			
	x	**y**	**z**	**Total**
Cadmium chloride	0.0004	0.0000	0	0.0004
Mercury iodide	-0.0001	0.0000	0.0000	0.0001
Mercury oxide	-0.9880	-4.4600	-0.9787	4.6718
Silver nitrate	-6.6813	-3.0202	1.4662	7.4774
Titanium dioxide	-6.4424	0.7161	2.4928	6.9449
Copper nitrate	0.0004	0.0005	-0.0001	0.0007

Table 4 : Frontier Molecular Orbital

Compound	eV											Q^{Max}
	HOMO	**LUMO**	**BG**	**IP**	**EA**	**ECP**	**CH**	**GS**	**EI**	**AEN**	
Cadmium chloride	-8.6315	-3.0912	5.5	8.6	3.1	-5.9	2.8	0.4	47.6	5.9	2.1
Mercury iodide	-7.5702	-3.3769	4.2	7.6	3.4	-5.5	2.1	0.5	31.4	5.5	2.6
Mercury oxide	-7.3716	-4.6069	2.8	7.4	4.6	-6.0	1.4	0.7	24.8	6.0	4.3
Silver nitrate	-7.3716	-3.9919	3.4	7.4	4.0	-5.7	1.7	0.6	27.3	5.7	3.4
Titanium dioxide	-7.162	-3.4967	3.7	7.2	3.5	-5.3	1.8	0.5	26.0	5.3	2.9
Copper nitrate	-8.1716	-5.2518	2.9	8.2	5.3	-6.7	1.5	0.7	32.9	6.7	4.6

BG-Band Gap; IP-Ionisation Potential; EA-Electron Affinity; ECP-Effective Core Potential; CH- Chemical hardness; GS- Global Softness; EI- Electrophilic index; AEN- Absolute Electronegativity

Table 5: Pearson's Correlation Coefficient

	HOMO	**LUMO**	**BG**	**MW**	**DEN**	**MPT**	**SOL**	**MS**	**BL**	**CM**	**CX**	**DM**
HOMO	1	0.417	0.261	-0.159	-0.477	-0.316	0.124	0.876	0.046	-0.013	-0.241	-0.697
LUMO	0.417	1	-0.731	-0.109	0.087	-0.367	0.162	0.731	-0.346	-0.392	-0.221	-0.294
BG	0.261	-0.731	1	0.264	-0.312	0.004	-0.218	-0.143	0.572	0.160	-0.056	-0.376
MW	-0.159	-0.109	0.264	1	0.280	-0.614	-0.255	-0.112	0.810	-0.863	-0.574	-0.561
DEN	-0.477	0.087	-0.312	0.280	1	-0.157	-0.468	-0.485	-0.008	-0.254	0.488	0.138
MPT	-0.316	-0.367	0.004	-0.614	-0.157	1	-0.349	-0.360	-0.712	0.760	0.591	0.564
SOL	0.124	0.162	-0.218	-0.255	-0.468	-0.349	1	0.237	0.138	0.056	-0.411	0.275
MS	0.876	0.731	-0.143	-0.112	-0.485	-0.360	0.237	1	-0.091	-0.246	-0.466	-0.640
BL	0.046	-0.346	0.572	0.810	-0.008	-0.712	0.138	-0.091	1	-0.588	-0.583	-0.488
CM	-0.013	-0.392	0.160	-0.863	-0.254	0.760	0.056	-0.246	-0.588	1	0.700	0.603
CX	-0.241	-0.221	-0.056	-0.574	0.488	0.591	-0.411	-0.466	-0.583	0.700	1	0.516
DM	-0.697	-0.294	-0.376	-0.561	0.138	0.564	0.275	-0.640	-0.488	0.603	0.516	1

MW-Molecular wt.; DEN-Density; MPT-Melting pt.; SOL-Solubility in water (25°C);MS-Magnetic susceptibility; BL-Bond length (Metal-non-metal); CM-Charge on Metal; CX- Charge on Non-Metal; DM-Dipole moment
2-tailes; 95% level of significance; M-metal; X-non-metal; very high- > 0.8; high- 0.79-0.6; Moderate-0.59-0.4; low-0.39-0.2;negligible -< 0.2